L2 1 JP08339081/PN

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L2 ANSWER 1 OF 1 JAPIO COPYRIGHT 1999 JPO
ACCESSION NUMBER: 1996-339081 . JAPIO
TITLE: PHOTOSENSITIVE RESIN COMPOSITION AND ITS PRODUCTION
INVENTOR: SATO HIROMITSU
PATENT ASSIGNEE(S): TOKYO OHKA KOGYO CO LTD, JP (CO 330196)
PATENT INFORMATION:

PATENT NO	KIND	DATE	ERA	MAIN IPC
JP 08339081	A19961224		Heisei (6)	G03F007-027

JP
APPLICATION INFORMATION
ST19N FORMAT: JP1995-167078 19950609
ORIGINAL: JP07167078 Heisei
SOURCE: PATENT ABSTRACTS OF JAPAN (CD-ROM), Unexamined Applications, Vol. 96, No. 12
INT. PATENT CLASSIF.:
MAIN: (6) G03F007-027
SECONDARY: (6) G03F007-038
ABSTRACT:

PURPOSE: To obtain a photosensitive resin compsn. excellent in heat and chemical resistances, excellent also in various characteristics such as adhesion to a substrate, developable with water or a dil. aq. alkali soln. and usable in many uses as an etching resist for forming a copper wiring pattern, a dry film resist, a soldering resist, etc., without adversely affecting working environment and natural environment.
CONSTITUTION: In this photosensitive resin compsn. contg. a photopoly-merizable resin and a photopolymn. initiator, the photopolymerizable resin is an addit.ion product obtd. by adding an unsatd. compd. having an .alpha.,.beta.-unsatd. double bond and an epoxy group to a resin having carboxyl groups and has an acid value of 50-200. The resin having carboxyl groups is produced by dissolving an ethylenically unsaid. acid monomer and a monomer copolymerizable with the acid monomer in an alcoholic solvent and bringing the resultant soln. into thermal polymn. in the presence of a thermal polymn. initiator.

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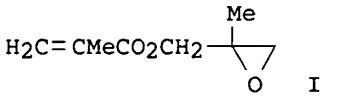
L4 ANSWER 1 OF 1 CA COPYRIGHT 1999 ACS
ACCESSION NUMBER: 126:205478 CA
TITLE: Photosensitive resin composition and its preparation
INVENTOR(S): Sato, Hiromitsu
PATENT ASSIGNEE(S): Tokyo Ohka Kogyo Co Ltd, Japan
SOURCE: Jpn. Kokai Tokkyo Koho, 13 pp.
CODEN: JKXXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
INT. PATENT CLASSIF.:
MAIN: G03F007-027
SECONDARY: G03F007-038
CLASSIFICATION: 74-5 (Radiation Chemistry, Photochemistry, and Photographic and Other Reprographic Processes)
Section cross-reference(s): 37
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 08339081	A2	19961224	JP 1995-167078	19950609 <--

GRAPHIC IMAGE:



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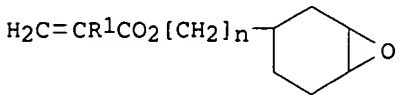
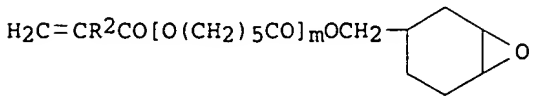


II



III

ABSTRACT:
The title resin compn. contains a photopolymn. initiator and a photopolymerizable resin with acid value 50-200, which is an adduct of a carboxyl-contg. resin and an unsatd. compd. having .alpha.,.beta.-unsatd. double bond and epoxy group. The unsatd. compd. may be .gtoreq.1 compd. selected from glycidyl (meth)acrylate and epoxy compds. I, II, and III (R1, R2 = H or Me; n = 1-10; m = 1-3). The compn. is prepd. by adding the unsatd. compd. to the carboxy-contg. resin obtained by thermally polymg. an ethylenic unsatd. acid monomers and copolymerizable monomers in an alc. solvent followed by mixing the photopolymn. initiator. The ethylenic unsatd. acid monomers may be .gtoreq.1 compd. selected from (meth)acrylic acid, (iso)crotonic acid, angelic acid, tiglic acid, 2-ethylacrylic acid, 3-(iso)propylacrylic acid, and .omega.-carboxypolycaprolactone mono(meth)acrylate. The compn. shows good thermal resistance, chem. resistance, and adhesion to substrates and is developable with water and dil. alk. aq. solns.

SUPPL. TERM: photoresist carboxylic resin epoxy acrylate
INDEX TERM: Photoresists
(photosensitive compn. contg. adduct of unsatd. epoxy

compd. and carboxylic acid resin)

INDEX TERM: Epoxy resin acrylates
ROLE: TEM (Technical or engineered material use); USES (Uses)
(photosensitive compn. contg. adduct of unsatd. epoxy compd. and carboxylic acid resin)

INDEX TERM: 107634-36-6P 187547-32-6P 187682-66-2P 187682-67-3P 187682-68-4P
ROLE: PNU (Preparation, unclassified); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)
(photosensitive compn. contg. adduct of unsatd. epoxy compd. and carboxylic acid resin)

INDEX TERM: 78-67-1, 2,2'-Azobisisobutyronitrile 2094-98-6, 1,1'-Azobis-(cyclohexane-1-carbonitrile) 4419-11-8, 2,2'-Azobis-(2,4-dimethylvaleronitrile) 13467-82-8, tert-Butyl peroctoate 187457-87-0
ROLE: CAT (Catalyst use); USES (Uses)
(thermal polymn. initiator in prepn. of carboxylic resin)

L7 1 JP08339081/PN

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L7 ANSWER 1 OF 1 WPIDS COPYRIGHT 1999 DERWENT INFORMATION LTD
ACCESSION NUMBER: 1997-104947 [10] WPIDS
DOC. NO. NON-CPI: N1997-086768
DOC. NO. CPI: C1997-033707
TITLE: Photosensitive resin compsn., e.g., for photoresist or printing plate - includes photopolymerising resin which is addn. prod. of carboxyl gp.-contg. resin and unsatd. cpd. having alpha, beta-unsatd. bond and epoxy gp..
DERWENT CLASS: A89 G06 L03 P84 V04
PATENT ASSIGNEE(S): (TOKQ) TOKYO OHKA KOGYO CO LTD
COUNTRY COUNT: 1
PATENT INFORMATION:

PATENT NO	KIND	DATE	WEEK	LA	PG	MAIN IPC
JP 08339081	A	19961224	(199710)*		13	G03F007-027<--

APPLICATION DETAILS:

PATENT NO	KIND	APPLICATION	DATE
JP 08339081	A	JP 1995-167078	19950609

PRIORITY APPLN. INFO: JP 1995-167078 19950609
INT. PATENT CLASSIF.:
MAIN: G03F007-027
SECONDARY: G03F007-038
BASIC ABSTRACT:
JP 08339081 A UPAB: 19970307
The photosensitive resin compsn. contains a photopolymerisation resin and a photopolymerisation initiator. The photopolymerisation resin is an additional product with a carboxyl gp. containing resin and an unsatd. cpd. which has an alpha, beta-unsatd. double bond and an epoxy gp. and an acid value of which is 50-200.

Also claimed is the mfr. of the photosensitive resin compsn. which comprises dissolving ethylenical unsatd. acid monomer and its copolymerising monomer into alcoholic solvent and synthesising the carboxyl gp.-containing resin by heat-polymerising and then adding the unsatd. cpd. which has an alpha, beta-unsatd. bond and epoxy gp. to mfr. the photopolymerisation resin compsn. and then combining the photopolymerisation initiator with the compsn..

USE - The photosensitive resin compsn. is used, e.g., for a photoresist solder resist or printing plate material.

ADVANTAGE - The photosensitive resin compsn. has improved heat and chemical resistance required for the photosensitive resin compsn. and also has improved characteristics such as adhesion with a substrate. It can be developed by water and dilute alkali aq. soln. so that the compsn. may be used for a resist for etching of a copper wiring pattern, a dry film resist, a solder resist and the like without negative effects on the surrounding environment.

Dwg.0/0
FILE SEGMENT: CPI EPI GMPI
FIELD AVAILABILITY: AB
MANUAL CODES: CPI: A10-E07; A11-C02B; A12-E07A; A12-L02B1; A12-L02B2; A12-W07B; A12-W07C; G05-A; G06-D04; G06-D05; G06-D06; G06-F03C; L03-H04E2; L04-C05
EPI: V04-R01A1; V04-R04A2

(6)

Tokyo Ohka

Japanese Patent Kokai (A) Hei 8-339081

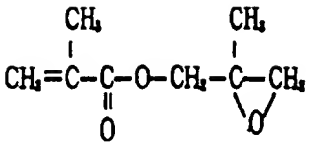
[Claims]

1. A photosensitive resin composition comprising a photopolymerizable resin and a photopolymerization initiator, characterized in that said photopolymerizable resin is an adduct of a carboxyl group-containing resin and an unsaturated compound having an α,β-unsaturated double bond and an epoxy group and said photopolymerizable resin has an acid value of 50-200.

2. The photosensitive resin composition claimed in Claim 1, wherein said photopolymerizable resin has an α,β-unsaturated double bond on the side chain thereof and has an acid value of 70-150 and a glass transition point of 30-120°C.

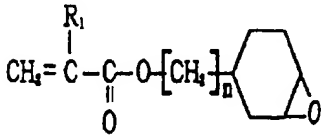
3. The photosensitive resin composition claimed in Claim1, wherein said unsaturated compound having an α,β-unsaturated double bond and an epoxy group is at least one member selected from the group consisting of glycidyl acrylate, glycidyl methacrylate, a compound of the following Formula 1:

[Formula 1]



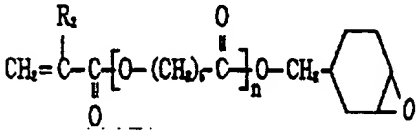
and alicyclic epoxy compounds represented by the following Formula 2 and Formula 3:

[Formula 2]



wherein R_1 is hydrogen atom or methyl group and n is an integer of 1-10,

[Formul 3]



wherein R_2 is hydrogen atom or methyl group and n is an integer of 1-3.

4. The photosensitive resin composition claimed in Claim 1, wherein said carboxyl group-containing resin is a polymer formed from an ethylenically unsaturated acid monomer and a copolymerizable monomer thereof.

5. The photosensitive resin composition claimed in Claim 4, wherein said ethylenically unsaturated acid monomer is at least one member selected from the group consisting of acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid, angelic acid, tiglic acid, 2-ethylacrylic acid, 3-propylacrylic acid, 3-isopropylacrylic acid, ω-carboxy-polycaprolactone monoacrylate and ω-carboxy-polycaprolactone monomethacrylate.

6. A process for producing a photosensitive resin composition comprising a photopolymerizable resin and a photopolymerization initiator, characterized by dissolving an

ethylenically unsaturated acid monomer and a copolymerizable monomer thereof in an alcoholic solvent, thermally polymerizing the solution to synthesize a carboxyl group-containing resin, then adding thereto an unsaturated compound having an α,β-unsaturated double bond and an epoxy group to produce a photopolymerizable resin composition, and subsequently compounding a photopolymerization initiator into said composition.

7. The process claimed in Claim 6, characterized by dissolving 70-95% by weight of an ethylenically unsaturated acid monomer and 5-30% by weight of a copolymerizable monomer thereof in an alcoholic solvent and carrying out a thermal polymerization at 45-120°C in the presence of a thermal polymerization initiator selected from 2,2'-azobis(2,4-dimethylvaleronitrile), 2,2'-azobisisobutyronitrile, 2,2'-azobis(2-methylisobutyronitrile), tert-butyl peroctoate, 1,1'-azobis(cyclohexane-1-carbonitrile) and 1-[(1-diazo-1-methylethyl)azo]-formamide.

8. The process claimed in Claim 7, characterized in that said alcoholic solvent is a solvent having at least one alcoholic OH group in molecule.

[Detailed Description of the Invention]

[Industrial Field of the Invention]

The present invention relates to a photosensitive resin composition and a process for production thereof, and more particularly to a photosensitive resin composition suitable for use as photoresist, solder resist, printing plate, etc. and a process for production thereof.

[Prior Art]

Photosensitive resin compositions comprising a polymeric binder, a photopolymerizable monomer and a photopolymerization initiator have so far been used as etching resist and solder resist for printed circuit boards

and for other metallic fabrications. When such a photosensitive resin composition is used for manufacture of printed circuit board, a high sensitivity, a high resolution and high chemical resistance, heat resistance, plating resistance and insulating property are required of the composition, and further the composition must have a high long-term storage stability before use. Furthermore, from the viewpoint of protection of working environment and natural environment, a composition which can easily be developed with water or dilute alkaline aqueous solution is desirable. As a photosensitive resin composition satisfying such requirements, an active energy-curable unsaturated resin composition produced by reacting a high acid value acrylic resin with an alicyclic epoxy group-containing compound is proposed in Japan. Pat. Kokai Hei 1-289819, and an active energy-curable unsaturated resin composition prepared by reacting an acid group-containing acrylic resin with an alicyclic epoxy group-containing unsaturated compound and compounding the reaction product with organic solvent and/or polymerizable vinyl monomer is proposed in Japan. Pat. Kokai Hei 1-289820.

[Problem to be Solved by the Invention]

However, in the above-mentioned active energy-curable unsaturated resin compositions, the high acid value acrylic resin is low in the content of carboxyl group. If the composition is reacted with an alicyclic epoxy group-containing unsaturated compound with the aim of enhancing its heat resistance, the product becomes difficult to develop with water or dilute alkaline aqueous solution, so that it must be used in the form of a solution in organic solvent. The use of organic solvent is undesirable from the viewpoint of protection of working environment and natural environment. With the aim of solving this problem, an attempt has been made to treat the active energy-curable unsaturated resin

composition with a polybasic acid anhydride such as phthalic anhydride to introduce carboxyl group into the side chain, or to incorporate a monomer into the composition to modify the composition so as to make it easily developable with water or dilute alkaline aqueous solution. The former technique, however, is undesirable because the synthesis involves many steps and is troublesome, or gelation of reaction mixture takes place in the process of synthesis. On the other hand, the latter technique is disadvantageous in that cold flow takes place in the state of dry film.

In order to develop a photosensitive resin composition free from the above-mentioned disadvantages, the present inventors have conducted extensive studies. As a result, it has been found that a photosensitive resin composition which can easily be developed with water or dilute alkaline aqueous solution while retaining high sensitivity, high resolution, high chemical resistance, high heat resistance and high plating resistance can be obtained by using, as the photopolymerizable resin in a photosensitive resin composition comprising a photopolymerizable resin and a photopolymerization initiator, a reaction product obtained by adding an unsaturated compound having an α,β-unsaturated double bond and an epoxy group to a specified carboxyl group-containing resin. It has further found that such a photopolymerizable resin can easily be obtained by thermally polymerizing an ethylenically unsaturated acid monomer and a copolymerizable monomer thereof in an alcoholic solvent to prepare a carboxyl group-containing resin having a high carboxyl group content and adding thereto an unsaturated compound having an α,β-unsaturated double bond an epoxy group. Based on these findings, the present invention has been accomplished.

Thus, it is an object of the present invention to provide a photosensitive resin composition excellent in sensitivity, resolution, flow property, chemical resistance, heat resistance, plating resistance, insulating property and long-term storage stability and easily developable with water or dilute alkaline aqueous solution.

It is another object of the present invention to provide a novel process for producing said photosensitive resin composition.

[Means for Solution of the Problem]

For achieving the object mentioned above, the present invention provides a photosensitive resin composition comprising a photopolymerizable resin and a photopolymerization initiator characterized in that said photopolymerizable resin is an adduct of a carboxyl group-containing resin and an unsaturated compound having an α,β-unsaturated double bond and an epoxy group and said photopolymerizable resin has an acid value of 50-200, and a process for producing said photosensitive resin composition.

As referred to herein, the term "photopolymerizable resin" means a resin having α,β-unsaturated double bonds on the side chains thereof, capable of being cured by the action of radiation in the presence of a photopolymerization initiator, and having an acid value of 50-200. The photopolymerizable resin is constituted of 70-95% by weight of an ethylenically unsaturated acid component and a copolymerizable component thereof. It is an addition product formed between a carboxyl group-containing resin having an acid value (the acid value is expressed by milligram number of potassium hydroxide necessary for neutralizing 1 gram of resin) of no less than 500, preferably no less than 600 and further preferably no less than 620 and having a number average molecular weight of 1,000-100,000, preferably 3,000-

70,000, and an unsaturated compound having an α,β-unsaturated double bond and an epoxy group. In the photosensitive resin composition containing the photopolymerizable resin, the content of the ethylenically unsaturated acid component in the carboxyl group-containing resin of the photopolymerizabe resin is 70-95% by weight, due to which the photopolymerizable resin does not become insoluble in water or dilute alkaline aqueous solution even after an unsaturated compound having an α,β-unsaturated double bond and an epoxy group is added thereto, and retains its solubility. If the content of the ethylenically unsaturated acid component in the carboxyl group-containing resin exceeds 95% by weight, impact resistance is deteriorated so that the result is not good. If the acid value is lower than 500, developability of the photopolymerizable resin becomes worse. If the average molecular weight exceeds 100,000, solubility in solvent is not good. Practically desirable range of the average molecular weight is 3,000 to 70,000.

The carboxyl group-containing resin is produced by dissolving 70-95% by weight, preferably 78-88% by weight and further preferably 80-85% by weight of an ethylenically unsaturated acid monomer and 5-30% by weight, preferably 22-12% by weight and further preferably 15-20% by weight of a copolymerizable monomer in an alcoholic solvent and thermally polymerizing the solution at 45-120°C in the presence of a thermal polymerization initiator. If the reaction temperature is lower than 45°C, the reaction velocity is too low. If the reaction temperature is higher than 120°C, the monomers can form a gel in the process of polymerization, so that such a temperature is undesirable. By the use of an alcoholic solvent, a carboxyl group-containing resin having an acid value of no less than 500 and a number average

molecular weight of 1,000-100,000 can be produced in a high safety and a high stability.

Specific examples of the ethylenically unsaturated monomer usable in the production of the carboxyl group-containing resin include acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid, angelic acid, tiglic acid, 2-ethylacrylic acid, 3-propylacrylic acid, 3-isopropylacrylic acid, succinic acid mono-hydroxyethylacrylate, phthalic acid mono-hydroxyethylacrylate, dihydrophthalic acid mono-hydroxyethylacrylate, tetrahydrophthalic acid mono-hydroxy-ethylacrylate, hexahydrophthalic acid monohydroxyethyl-acrylate, acrylic acid dimer, acrylic acid trimer, ω-carboxy-polycaprolactone monoacrylate and ω-carboxy-polycaprolactone monomethacrylate. Among these monomers, preferred are acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid, angelic acid, tiglic acid, 2-ethylacrylic acid, 3-propylacrylic acid, 3-isopropylacrylic acid, ω-carboxy-polycaprolactone monoacrylate, ω-carboxy-polycaprolactone monomethacrylate, and the like; and particularly preferred are acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid, angelic acid, tiglic acid, 2-ethylacrylic acid, 3-propylacrylic acid, 3-isopropylacrylic acid, ω-carboxy-polycaprolactone monoacrylate, and ω-carboxy-polycaprolactone monomethacrylate. These monomers may be used either alone or in mixture of two or more.

As the copolymerizable monomers, acrylic esters, methacrylic esters, vinyl monomers, styrene type monomers and cyclic ester monomers can be referred to. Specific examples thereof include 2-hydroxymethyl acrylate, 2-hydroxymethyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, ethyleneglycol monomethyl ether acrylate, ethyleneglycol monomethyl ether methacrylate, ethyleneglycol

monoethyl ether acrylate, ethyleneglycol monoethyl ether methacrylate, glycerol acrylate, glycerol methacrylate, dipentaerythritol pentamethacrylate, dipentaerythritol pentaacrylate, dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, tetrahydrofurfuryl acrylate, tetrahydrofurfuryl methacrylate, acrylic acid amide, methacrylic acid amide, acrylonitrile, methacrylonitrile, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, isobutyl acrylate, isobutyl methacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl-methacrylate, benzyl acrylate, benzyl methacrylate, acrylic acid carbitol, methacrylic acid carbitol, ε-caprolactone-modified tetrafurfuryl acrylate, ε-caprolactone-modified tetrafurfuryl methacrylate, diethyleneglycol ethoxyl acrylate, isodecyl acrylate, isodecyl methacrylate, octyl acrylate, octyl methacrylate, lauryl acrylate, lauryl methacrylate, tridecyl acrylate, tridecyl methacrylate, stearyl acrylate, stearyl methacrylate and the like. These monomers may be used either alone or in mixture of two or more.

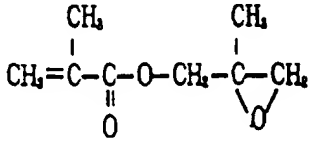
As the thermal polymerization initiator, 2,2′-azobis-(2,4-dimethylvaleronitrile) (usable temperature 45-70°C), 2,2′-azobis(isobutyronitrile) (usable temperature 60-90°C), 2,2′-azobis(2-methylisobutyronitrile) (usable temperature 60-95°C), tert-butyl peroctoate (usable temperature 75-100°C), 1,1′-azobis(cyclohexane-1-carbonitrile) (usable temperature 80-110°C), 1-[(1-diazo-1-methylethyl)azo]-formamide (usable temperature 95-120°C) can be referred to, and at least one of them is used.

As the alcoholic solvent, compounds having at least one OH group in molecule are used. Specific examples thereof include n-propanol, n-butanol, n-hexanol, n-heptanol, n-octanol, sec-butyl alcohol, tert-butyl alcohol, 2-

ethylbutanol, ethylhexanol, cyclohexanol, methylisobutylcarbinol, n-amyl alcohol, allyl alcohol, lauryl alcohol, benzyl alcohol, furfuryl alcohol, 1,3-butanediol, 2,3-butanediol, 1,5-pentanediol, 2,4-pentanediol, 2,5-hexanediol, 2-methyl-1,3-pentanediol, 2-methyl-2,4-pentanediol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethyleneglycol monobutyl ether, ethyleneglycol monobenzyl ether, ethyleneglycol monophenyl ether, diethyleneglycol monoethyl ether, diethyleneglycol monobutyl ether, propylene glycol monomethyl ether, propylene glycol monoethyl ether, dipropylene glycol monomethyl ether and dipropylene glycol monoethyl ether. Among these solvents, preferred are propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol monopropyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, dipropylene glycol monopropyl ether and the like. The use of polyhydric alcohols is preferable from the viewpoint of stability of resin quality. These solvents may be used either alone or in mixture of two or more.

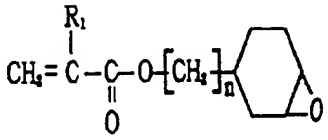
The carboxyl group-containing resin produced according to the aforementioned method is then modified into a photopolymerizable resin of which carboxyl group is esterified and of which side chains have α,β-unsaturated double bonds, through an esterification with an unsaturated compound having an α,β-unsaturated double bond and a epoxy group. As the compound having an α,β-unsaturated double bond and an epoxy group, at least one member selected from the group consisting of glycidyl acrylate, glycidyl methacrylate, the compound of Formula 4:

[Formula 4]



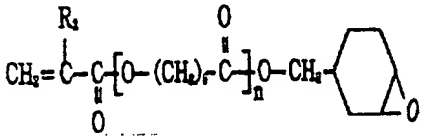
and alicyclic compounds represented by the following Formulas 5 and 6:

[Formula 5]



wherein R_1 is hydrogen atom or methyl group and n is an integer of 1-10,

[Formula 6]



wherein R_2 is hydrogen atom or methyl group and n is an integer of 1-3, can be referred to. Among these compounds, compounds having alicyclic epoxy group are particularly preferred, because these compounds have a high reactivity with carboxyl group-containing resin so that the reaction time can be shortened and do not cause gelation in the process of reaction and make it possible to carry out the reaction stably. On the other hand, glycidyl acrylate and glycidyl methacrylate are advantageous from the viewpoint of sensitivity and heat resistance because they have a low molecular weight and can give a high conversion of esterification.

The photopolymerizable resin obtained by the above-mentioned method has α,β-unsaturated double bonds on its side chains. Its acid value is 50-200, preferably 70-150, and further preferably 85-120. Its number average molecular weight is 7,000-10,000, and its glass transition point (hereinafter referred to as Tg) is 30-120°C. If acid value of the resin is lower than 50, development takes too long a period of time. If the acid value is higher than 200, water resistance is not good. If Tg of the photopolymerizable

resin is lower than 30°C, tackiness is too high, so that contact exposure cannot be carried out. If Tg is higher than 120°C, adhesiveness to substrate is not good and plating resistance is low. When the photopolymerizable resin is used as a solder resist, an acid value of no less than 70 is preferable because other additive ingredients may further be added to the composition.

An inert organic solvent is used at the time of carrying out the esterification and preparing the photosensitive resin composition. Specific examples of the inert organic solvent include the alcoholic solvents mentioned above and, in addition, acetate solvents such as 2-methoxybutyl acetate, 3-methoxybutyl acetate, 4-methoxybutyl acetate, 2-methyl-3-methoxybutyl acetate, 3-methyl-3-methoxybutyl acetate, 3-ethyl-3-methoxybutyl acetate, 2-ethoxybutyl acetate, 4-ethoxybutyl acetate, 4-propoxybutyl acetate, 2-methoxypentyl acetate, 3-methoxypentyl acetate, 4-methoxypentyl acetate, 2-methyl-3-methoxypentyl acetate, 3-methyl-3-methoxypentyl acetate, 3-methyl-4-methoxypentyl acetate, 4-methyl-4-methoxypentyl acetate, methyl lactate, ethyl lactate, methyl acetate, ethyl acetate, propyl acetate, butyl acetate, methyl propionate, ethyl propionate and the like; ketone solvents such as methyl ethyl ketone, acetone, methyl isobutyl ketone, diethyl ketone, cyclohexanone and the like; and compounds having an α,β-unsaturated double bond and an epoxy group in molecule. Of these solvents, alcoholic solvents are particularly preferred from the viewpoint of efficiency of production. These solvents may be used either alone or in combination of two or more.

The photosensitive resin composition of the present invention comprises the above-mentioned photopolymerizable resin and a photopolymerization initiator. Specific examples of the photopolymerization initiator include 1-

hydroxycyclohexyl phenyl ketone, 2,2-dimethoxy-1,2-diphenylethan-1-one, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one, 2-hydroxy-2-methyl-1-phenylpropan-1-one, 2,4,6-trimethylbenzoyldiphenylphosphine oxide, 1-[4-(2-hydroxyethoxy)phenyl]-2-hydroxy-2-methyl-1-propan-1-one, 2,4-diethylthioxanthone, 2-chlorothioxanthone, 2,4-dimethylthioxanthone, 3,3-dimethyl-4-methoxybenzophenone, benzophenone, 1-chloro-4-propoxythioxanthone, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one, 1-(4-dodecylphenyl)-2-hydroxy-2-methylpropan-1-one, 4-benzoyl-4'-methyl-dimethyl sulfide, 4-dimethylaminobenzoic acid, methyl 4-dimethylaminobenzoate, ethyl 4-dimethylaminobenzoate, butyl 4-dimethylaminobenzoate, 2-ethylhexyl 4-dimethylamino-benzoate, 2-isoamyl 4-dimethylaminobenzoate, 2,2-diethoxy-acetophenone, benzyl dimethyl ketal, benzyl-β-methoxyethyl acetal, 1-phenyl-1,2-propandione-2-(o-ethoxycarbonyl) oxime, methyl o-benzoylbenzoate, bis(4-methylaminophenyl) ketone, 4,4'-bisdiethylamino-benzophenone, 4,4'dichlorobenzophenone, benzil, benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin n-butyl ether, benzoin isobutyl ether, p-dimethylaminoacetophenone, p-tert-butyltrichloroacetophenone, p-tert-butyldichloroacetophenone, thioxanthone, 2-methylthioxanthone, 2-isopropylthioxanthone, dibenzosuberone, α,α-dichloro-4-phenoxyacetophenone, pentyl -4-dimethylaminobenzoate and the like. These initiators may be used either alone or in mixture of two or more. The content of the photopolymerization initiator is 0.1-20 parts by weight per 100 parts by weight of solid component in the photosensitive resin composition. If the quantity of the photopolymerization initiator is smaller than 0.1 part by weight, the photo-cure cannot progress sufficiently, and the product is inferior in heat resistance and chemical

resistance. If its quantity is larger than 20 parts by weight, adhesiveness is not good.

Into the photosensitive resin composition of the present invention, known photopolymerizable polyfunctional monomer, polymerizable prepolymer, epoxy resin and curing agent may be appropriately incorporated in accordance with the use of the composition and the desired properties of coating film, and tackiness improver, antifoaming agent, thermal polymerization inhibitor and filler may also be added so far as their addition does not affect the curability.

Specific examples of the photopolymerizable polyfunctional monomer include monofunctional monomers such as 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, ethyleneglycol monoethyl ether acrylate, ethyleneglycol monomethyl ether methacrylate, ethyleneglycol monoethyl ether acrylate, ethyleneglycol monoethyl ether methacrylate, glycerol acrylate, glycerol methacrylate, acrylamide, methacrylamide, acrylonitrile, methacrylonitrile, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, isobutyl acrylate, isobutyl methacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, benzyl acrylate, benzyl methacrylate and the like; as well as ethyleneglycol diacrylate, ethyleneglycol dimethacrylate, triethyleneglycol diacrylate, triethyleneglycol dimeth-acrylate, tetraethyleneglycol diacrylate, tetraethyleneglycol dimethacrylate, butyleneglycol dimethacrylate, propylene-glycol diacrylate, propyleneglycol dimethacrylate, trimethylol-propane triacrylate, trimethylolpropane trimethacrylate, tetramethylolpropane tetraacrylate, tetramethylolpropane tetramethacrylate, pentaerythritol triacrylate, pentaerythritol trimethacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, dipentaerythritol pentaacrylate, dipentaerythritol pentamethacrylate, dipentaerythritol hexaacrylate,

dipentaerythritol hexamethacrylate, 1,6-hexanediol diacrylate, 1,6-hexanediol hexamethacrylate, cardoepoxy diacrylate and the like. As the polymerizable prepolymer, a resin prepared by introducing hydroxyalkyl (meth)acrylate into carboxyl group-containing polyol through intermediation of a polyisocyanate compound, (meth)acrylic esters of polyester-polyol, and the like can be referred to. One or two or more members of the photopolymerizable monomer and the photopolymerizable prepolymer can be incorporated in an amount of 1-50 parts by weight per 100 parts by weight of the solid component in the photosensitive resin composition. The amount of photopolymerizable monomer must be carefully controlled, because a photosensitive resin composition containing a photopolymerizable monomer tends to show cold flow in the state of dry film.

As the epoxy resin used as an optional ingredient, Bisphenol A type epoxy resin, Bisphenol F type epoxy resin, Bisphenol S type epoxy resin, phenol novolak type epoxy resin, cresol novolak type epoxy resin, condensate of a phenol and a phenolic hydroxyl group-containing aromatic aldehyde, and triazine resins such as tris(2,3-diepoxypropyl) isocyanurate and the like can be referred to. As the epoxy curing agent, amine type epoxy curing agents, cationic epoxy curing agent and the like can be used.

Further, as tackiness improver, copolymers having carboxyl groups and N-alkoxyacrylamide groups, compounds prepared by reacting hydroxyethyl methacrylate with a styrene-maleic anhydride copolymer, and the like can be used. As the antifoaming agent, silicone compounds and fluorine compounds can be used. As the thermal polymerization inhibitor, hydroquinone, hydroquinone monomethyl ether and the like and bisphenol type inhibitors can be used. As the pigment, Phthalocyanine Blue, Phthalocyanine Green, titanium oxide, carbon black and the like can be used. As the filler,

silica, talc, barium sulfate, calcium carbonate, clay, silicic acid hydrate, aluminum hydroxide, aluminum oxide, antimony trioxide, magnesium carbonate, aluminum silicate, magnesium silicate, aerosil and the like having particle diameter of 0.001-10 μm can be used.

As the method for forming a coating film from the photosensitive resin composition of the invention, for example, a method of adding a photopolymerizable polyfunctional monomer, a filler, a thermal polymerization inhibitor and the like to a photosensitive resin composition comprising a photopolymerizable resin and a photopolymerization initiator, thoroughly kneading the composition thus obtained with triple roll mill, ball mill, sand mill or the like to prepare a photosensitive resin composition, coating a substrate made of plastic, metal or inorganic material and particularly a laminate constituted of glass fiber layer and epoxy resin layer with the composition by means of roll coater, reverse coater, spinner, curtain flow coater, spray or the like, drying the coating at room temperature or in a hot air heater, exposing the coating film to a high energy beam using high-pressure mercury lamp, super-high pressure mercury lamp, xenon lamp, metal halide lamp or the like through a negative mask, and developing the film by means of spray gun, immersion method or padding method to form a coating film such as resist pattern or the like having a dry film thickness of 5-150 μm, preferably 10-70 μm, can be adopted. If film thickness of the dry coating film exceeds 150 μm, the water present in the film cannot be removed, which deteriorates curability of the film.

For developing the coating film formed from the photosensitive resin composition of the invention, water or a dilute alkaline aqueous solution is used. Specific examples of the alkali component used in the dilute alkaline aqueous

solution include hydroxides, carbonates, bicarbonates, phosphates and pyrophosphates of alkali metals; primary amines such as benzylamine, butylamine and the like; secondary amines such as dimethylamine, dibenzylamine, diethanolamine and the like; tertiary amines such as trimethylamine, triethylamine, triethanolamine and the like; cyclic amines such as morpholine, piperazine, pyridine and the like; polyamines such as ethylenediamine, hexamethylene-diamine and the like; ammonium hydroxides such as tetraethylammonium hydroxide, trimethylbenzylammonium hydroxide, trimethylphenylbenzylammonium hydroxide, choline and the like; sulfonium hydroxides such as trimethylsulfonium hydroxide, diethylmethylsulfonium hydroxide and the like; and mixtures of these alkali components and buffer solutions. These alkali components may be used either alone or in mixture of two or more.

The coating film having been developed as above is further dried or post-baked at 100-200°C for 10 minutes to 3 hours, if desired. By this treatment, the polymerization and cure of the coating film can be made to progress additionally, and heat resistance, etching resistance and adhesive property can be improved.

The photosensitive resin composition of the present invention is used as coating material, printing ink, photoresist, solder resist, printing plate material and the like. Particularly when it is used as a dry film resist for forming a circuit of printed circuit board, it is recommendable to use a method of coating the photosensitive resin composition of the invention on a flexible film of polyethylene or polyester by the use of applicator, bar coater, roll coater, curtain flow coater or the like so as to give the coating a dry thickness of 10-100 μm, drying the coating film, and laminating thereon a mold release film to

give a dry film resist. As the mold release film, polyethylene film and the like are preferable, and the mold release film is useful for stabilizing and protecting the photosensitive resin layer before use. As the base film for resist coating, polyester film or the like is used. In the preparation of dry film resist, a water-soluble resin layer may be provided between the photosensitive resin layer and the flexible film in order to prevent the oxygen-desensitization of photosensitive resin and sticking of mask (pattern) used at the time of exposure. Said water-soluble resin layer is prepared by coating a 5-20% by weight aqueous solution of a water-soluble polymer such as polyvinyl alcohol, partially saponified polyvinyl acetate or the like by means of bar coater, roll coater, curtain flow coater so as to give a dry thickness of 1-10 μm, and drying the coating.

In putting the dry film resist to use, the following procedure is recommendable. Thus, mold release film is peeled off from the dry film resist, the exposed photosensitive resin layer is placed on a hot substrate surface, a pressure is applied from the base film side to bring the two materials into a sufficient bonding, then superposing a prescribed negative mask on the photosensitive resin layer, and then exposure, development and drying are performed. By using the dry resist film obtained in this manner, good circuits of printed circuit board can be formed.

[Examples]

Next, the invention is further explained by referring to the following "Synthesis Examples of Photopolymerizable Resin" and "Examples". The invention is by no means limited by these examples.

Synthesis Example 1 of Photopolymerizable Resin

A mixed solution consisting of 72 parts by weight of acrylic acid, 10 parts by weight of methyl methacrylate, 6.5

parts by weight of 2-hydroxyethyl methacrylate and 2 parts by weight of 2,2'-azobisisobutyronitrile was dropped into 100 parts by weight of propyleneglycol monomethyl ether kept at 80°C, over a period of 2 hours in an atmosphere of nitrogen gas, after which the resulting mixture was kept at that temperature for an additional 8 hours to make progress a polymerization reaction. A part of the reaction mixture was sampled out, and acid value, number average molecular weight and Tg were measured. The results were 634, 8,400 and 99°C, respectively.

Into the polymer solution obtained above were dropped at 80°C 100 parts by weight of glycidyl methacrylate and 90 parts by weight of propyleneglycol monomethyl ether over a period of one hour, after which the resulting mixture was further reacted for 4 hours. Thus, a photopolymerizable resin having α,β-unsaturated double bonds on side chains thereof was obtained. Acid value, number average molecular weight and Tg of the resin were 93, 20,800 and 69°C, respectively.

Synthesis Example 2 of Photopolymerizable Resin

A carboxyl group-containing resin was prepared by polymerizing 36 parts by weight of acrylic acid, 43 parts by weight of methacrylic acid, 10 parts by weight of methyl methacrylate, 2 parts by weight of 2-hydroxyethyl methacrylate, 2 parts by weight of benzyl methacrylate and 2 parts by weight of 2,2'-azobis(2,4-dimethylvaleronitrile) in the same manner as in Synthesis Example 1, except that the reaction temperature was 55°C. A part of the reaction mixture was taken out to measure acid value, number average molecular weight and Tg. The results were 602, 9,800 and 158°C.

Into the polymer solution were dropped 71 parts by weight of glycidyl methacrylate, 31 parts by weight of (2-

methylglycidyl) methacrylate, 85 parts by weight of propyleneglycol monoethyl ether and 1 part by weight of 1,1'-azobis(cyclohexane-1-carbonitrile) at 100°C over a period of one hour, after which the mixture was kept at that temperature for 4 hours. Acid value, number average molecular weight and Tg of the photopolymerizable resin thus obtained were 101, 22,700 and 134°C, respectively.

Synthesis Example 3 of Photopolymerizable Resin

A carboxyl group-containing resin was prepared by polymerizing 72 parts by weight of acrylic acid, 9 parts by weight of benzyl methacrylate, 5 parts by weight of 2-hydroxyethyl methacrylate and 2 parts by weight of 1-[(1-diazo-1-methylethyl)azo]-formamide in the same manner as in Synthesis Example 1, except that the reaction temperature was 115°C. A part of the reaction mixture was taken out to measure acid value, number average molecular weight and Tg. The results were 648, 8,600 and 95°C.

Into the polymer solution were dropped 88 parts by weight of glycidyl acrylate and 90 parts by weight of dipropyleneglycol monopropyl ether at 115°C over a period of one hour, after which the mixture was kept at that temperature for 3 hours. Acid value, number average molecular weight and Tg of the photopolymerizable resin thus obtained were 96, 17,400 and 66°C, respectively.

Synthesis Example 4 of Photopolymerizable Resin

A carboxyl group-containing resin was prepared by polymerizing 64.8 parts by weight of acrylic acid, 20 parts by weight of ω-carboxy-polycaprolactone monomethacrylate, 4 parts by weight of methyl methacrylate, 4 parts by weight of 2-hydroxyethyl methacrylate and 2 parts by weight of 2,2'-azobisisobutyronitrile in the same manner as in Synthesis Example 1. A part of the reaction mixture was taken out to

measure acid value, number average molecular weight and Tg. The results were 602, 9,500 and 105°C.

Into the polymer solution were dropped 137 parts by weight of 3,4-oxocyclohexylethyl methacrylate and 100 parts by weight of propyleneglycol monoethyl ether at 80°C over a period of one hour, after which the mixture was kept at that temperature for 2.5 hours. Acid value, number average molecular weight and Tg of the photopolymerizable resin thus obtained were 84, 23,300 and 97°C, respectively.

Synthesis Example 5 of Photopolymerizable Resin

A carboxyl group-containing resin was prepared by polymerizing 72 parts by weight of acrylic acid, 10 parts by weight of methyl methacrylate, 6.5 parts by weight of 2-hydroxyethyl methacrylate and 2 parts by weight of 2,2'-azobisisobutyronitrile in the same manner as in Synthesis Example 1. A part of the reaction mixture was taken out to measure acid value, number average molecular weight and Tg. The results were 634, 8,400 and 99°C.

Into the polymer solution were dropped 38.4 parts by weight of glycidyl acrylate, 108 parts by weight of (3,4-oxocyclohexylmethyl)-caprolactone methacrylate and 100 parts by weight of propyleneglycol monoethyl ether at 80°C over a period of one hour, after which the mixture was kept at that temperature for 3 hours. Acid value, number average molecular weight and Tg of the photopolymerizable resin thus obtained were 83, 22,300 and 85°C, respectively.

Comparative Synthesis Example 1 of Photopolymerizable Resin

A mixture consisting of 72 parts by weight of acrylic acid, 10 parts by weight of methyl methacrylate, 6.5 parts by weight of 2-hydroxyethyl methacrylate and 2 parts by weight of 2,2'-azobisisobutyronitrile was dropped into 100 parts by weight of ethyleneglycol monoethyl ether acetate kept at 80°C over a period of 2 hours, after which the resulting mixture

was kept at that temperature for 16 hours to make progress a polymerization reaction. Acid value, number average molecular weight and Tg of the resin were 621, 3,400 and 100°C, respectively.

Into the solution obtained above were dropped 100 parts by weight of glycidyl methacrylate and 90 parts by weight of propyleneglycol monoethyl ether at 100°C over a period of one hour, after which the resulting mixture was kept at that temperature for 8 hours to obtain a photo-polymerizable resin. Acid value, number average molecular weight and Tg of the resin were 69, 4,820 and 69°C, respectively. No polymer having a higher degree of polymerization than the above could be obtained.

Comparative Synthesis Example 2 of Photopolymerizable Resin

Into 100 parts by weight of triethyleneglycol monoethyl ether kept at 130°C were dropped 72 parts by weight of acrylic acid, 10 parts by weight of methyl methacrylate, 6.5 parts by weight of 2-hydroxyethyl methacrylate and 2 parts by weight of 2-phenylazo-4-methoxy-2,4-dimethyl-valeronitrile over a period of one hour, and then polymerization was carried out at that temperature. As a result, the reaction mixture formed a gel, so that the reaction could not be continued further and the product could not be used for preparation of photosensitive resin composition.

Comparative Synthesis Example 3 of Photopolymerizable Resin

Into 100 parts by weight of ethyleneglycol monoethyl ether kept at 80°C were dropped 60 parts by weight of acrylic acid, 20 parts by weight of butyl methacrylate, 20 parts by weight of styrene and 2 parts by weight of 2,2'-azobisiso-butyronitrile over a period of 2 hours, and polymerization was carried out at that temperature for 8 hours. Acid value,

molecular weight and Tg were 465, 7,900 and 85°C, respectively.

At 80°C, 110 parts by weight of 3,4-oxocyclohexyl-ethyl methacrylate and 80 parts by weight of ethyleneglycol monoethyl ether were dropped into the reaction mixture obtained above over a period of one hour, and the resulting mixture was reacted for 4 hours. Acid value, molecular weight and Tg of the photopolymerizable resin thus obtained were 81, 17,750 and 66°C, respectively.

Comparative Synthesis Example 4 of Photopolymerizable Resin

Into 100 parts by weight of ethyleneglycol monoethyl ether kept at 80°C were dropped 60 parts by weight of acrylic acid, 20 parts by weight of butyl methacrylate, 20 parts by weight of styrene and 2 parts by weight of 2,2'-azobisisobutyronitrile over a period of 2 hours, and polymerization was carried out at that temperature for 8 hours. Acid value, molecular weight and Tg were 461, 8,100 and 85°C, respectively.

At 80°C, 133 parts by weight of 3,4-oxocyclohexyl-ethyl methacrylate and 90 parts by weight of ethyleneglycol monoethyl ether were dropped into the reaction mixture obtained above over a period of one hour, and the resulting mixture was reacted for 4 hours. Acid value, molecular weight and Tg of the photopolymerizable resin thus obtained were 47, 19,300 and 64°C, respectively.

Example 1

To 100 parts by weight of the solution of "Synthesis Example 1 of Photopolymerizable Resin" were added 2 parts by weight of 2-methyl-[4-(methylthio)phenyl]-2-morpholino-1-propane (trade name Irgacure 907, manufactured by Ciba Geigy), 2 parts by weight of diethylthioxanthone (trade name Cayacure DTEX, manufactured by Nippon Kayaku), 1 part by weight of isoamyl p-methylaminobenzoate (trade name Cayacure

DMBI, manufactured by Nippon Kayaku), 2 parts by weight of Phthalocyanine Green pigment and 1 part by weight of antifoaming agent. Kneading using a triple roll mill gave a photosensitive resin composition. The composition was coated on a substrate by means of a roll coater, dried at 80°C for 20 minutes, contacted with a negative mask, and exposed to the light of super-high pressure mercury lamp at an exposure amount of 400 mJ/cm^2. The unexposed portion was eliminated with 1% (by weight) aqueous solution of sodium carbonate to form a resist pattern. On the resist pattern thus obtained, percentage of residual film, developability and etching resistance were evaluated. Further, stability change in the lapse of time of the photosensitive resin composition was also measured. The results are shown in Table 1.

Example 2

To 100 parts by weight of the solution of "Synthesis Example 2 of Photopolymerizable Resin" were added 2 parts by weight of 2-methyl-[4-(methylthio)phenyl]-2-morpholino-1-propane (trade name Irgacure 907, manufactured by Ciba Geigy), 2 parts by weight of diethylthioxanthone (trade name Cayacure DTEX, manufactured by Nippon Kayaku), 1 part by weight of isoamyl p-methylaminobenzoate (trade name Cayacure DMBI, manufactured by Nippon Kayaku), 2 parts by weight of Phthalocyanine Green pigment, 1 part by weight of antifoaming agent, 2 parts by weight of polysiloxane compound (trade name KS-66, manufactured by Shin'etsu Kagaku), 5 parts by weight of Bisphenol A type epoxy resin (trade name EPICLON-850, manufactured by Dainippon Ink Chemical), 15 parts by weight of talc, 40 parts by weight of barium sulfate and 2 parts by weight of finely powdered silica (trade name Aerosil #200, manufactured by Nippon Aerosil). A solder resist pattern was formed in the same manner as in Example 1. The resist pattern was further heat-cured at 150°C for 60 minutes. On

the solder resist pattern thus obtained, percentage of residual film, developability, alkali resistance, solder heat resistance and solvent resistance were evaluated. Further, stability change in the lapse of time of the photosensitive resin composition was measured, and adhesive property was evaluated on a film prepared by coating the photosensitive resin composition in the same manner as in Example 1, followed by drying and whole area exposure to light. The results are shown in Table 1.

Example 3

To 100 parts by weight of the solution of "Synthesis Example 3 of Photopolymerizable Resin" were added 2 parts by weight of 2-methyl-[4-(methylthio)phenyl]-2-morpholino-1-propane (trade name Irgacure 907, manufactured by Ciba Geigy), 2 parts by weight of diethylthioxanthone (trade name Cayacure DTEX, manufactured by Nippon Kayaku), 1 part by weight of isoamyl p-methylaminobenzoate (trade name Cayacure DMBI, manufactured by Nippon Kayaku), 2 parts by weight of Phthalocyanine Green pigment and 1 part by weight of antifoaming agent. After kneading the composition with a triple roll, the composition was coated on a 0.03 mm polyester (PET) film with applicator so as to give a dry film thickness of 50 μm ad dried at 80°C for 20 minutes to obtain a dry film resist. The dry film resist was thermally contact-bonded on a substrate with laminator, and exposed to light and developed in the same manner as in Example 1 to form a solder resist pattern. On the resist pattern thus obtained, percentage of residual film, developability and etching resistance were evaluated. Further, stability change with time of the dry film was measured. Further, dry film resist was thermally contact-bonded to substrate and wholly exposed to light, and its adhesive property was measured. The results are shown in Table 1.

Example 4

To 100 parts by weight of the solution of "Synthesis Example 4 of Photopolymerizable Resin" were added 2 parts by weight of 2-methyl-[4-(methylthio)phenyl]-2-morpholino-1-propane (trade name Irgacure 907, manufactured by Ciba Geigy), 2 parts by weight of diethylthioxanthone (trade name Cayacure DTEX, manufactured by Nippon Kayaku), 1 part by weight of isoamyl p-methylaminobenzoate (trade name Cayacure DMBI, manufactured by Nippon Kayaku), 2 parts by weight of Phthalocyanine Green pigment, 1 part by weight of antifoaming agent, 2 parts by weight of polysiloxane compound (trade name KS-66, manufactured by Shin'etsu Kagaku), 5 parts by weight of Bisphenol A type epoxy resin (trade name EPICLON-850, manufactured by Dainippon Ink Chemical), 15 parts by weight of talc, 40 parts by weight of barium sulfate and 2 parts by weight of finely powdered silica (trade name Aerosil #200, manufactured by Nippon Aerosil). After kneading the composition with a triple roll, the composition was coated on a 0.03 mm polyester (PET) film with applicator so as to give a dry film thickness of 50 μm and dried at 80°C for 20 minutes to obtain a dry film solder resist. The dry film solder resist was thermally contact-bonded on a substrate by means of a laminator and exposed to light and developed in the same manner as in Example 1 to prepare a solder resist pattern. On the resist pattern thus obtained, percentage of residual film, developability, alkali resistance, solder heat resistance and solvent resistance were evaluated. Further, stability change in the lapse of time of the dry film solder resist was measured, and adhesive property was evaluated on a film prepared by thermally contact-bonding the dry film solder resist to a substrate and wholly exposing it to light. The results are shown in Table 1.

Example 5

To 100 parts by weight of the solution of "Synthesis Example 5 of Photopolymerizable Resin" were added 2 parts by

weight of 2-methyl-[4-(methylthio)phenyl]-2-morpholino-1-propane (trade name Irgacure 907, manufactured by Ciba Geigy), 2 parts by weight of diethylthioxanthone (trade name Cayacure DTEX, manufactured by Nippon Kayaku), 1 part by weight of isoamyl p-methylaminobenzoate (trade name Cayacure DMBI, manufactured by Nippon Kayaku), 5 parts by weight of trimethylolpropane triacrylate, 2 parts by weight of Phthalocyanine Green pigment and 1 part by weight of antifoaming agent. Kneading using a triple roll gave a photosensitive resin composition. The composition was coated, dried, exposed and developed in the same manner as in Example 1 to form a resist pattern. On the resist pattern thus obtained, percentage of residual film, developability and etching resistance were evaluated. Further, stability change in the lapse of time of the photosensitive resin composition was also measured. The results are shown in Table 1.

Comparative Example 1

To 100 parts by weight of the solution of "Comparative Synthesis Example 3 of Photopolymerizable Resin" were added 2 parts by weight of 2-methyl-[4-(methylthio)-phenyl]-2-morpholino-1-propane (trade name Irgacure 907, manufactured by Ciba Geigy), 2 parts by weight of diethylthioxanthone (trade name Cayacure DTEX, manufactured by Nippon Kayaku), 1 part by weight of isoamyl p-methyl-aminobenzoate (trade name Cayacure DMBI, manufactured by Nippon Kayaku), 2 parts by weight of Phthalocyanine Green pigment and 1 part by weight of antifoaming agent. Kneading using a triple roll gave a photosensitive resin composition. The composition was coated on a substrate by means of a roll coater, dried at 80°C for 20 minutes, contacted with a negative mask, and exposed to the light of super-high pressure mercury lamp at an exposure amount of 400 mJ/cm^2. The unexposed portion was eliminated with 1% (by weight)

aqueous solution of sodium carbonate to form a resist pattern. On the resist pattern thus obtained, percentage of residual film, developability and etching resistance were evaluated. Further, stability change in the lapse of time of the photosensitive resin composition was also measured. The results are shown in Table 1.

Comparative Example 2

To 100 parts by weight of the solution of "Comparative Synthesis Example 3 of Photopolymerizable Resin" were added 2 parts by weight of 2-methyl-[4-(methylthio)-phenyl]-2-morpholino-1-propane (trade name Irgacure 907, manufactured by Ciba Geigy), 2 parts by weight of diethylthioxanthone (trade name Cayacure DTEX, manufactured by Nippon Kayaku), 1 part by weight of isoamyl p-methyl-aminobenzoate (trade name Cayacure DMBI, manufactured by Nippon Kayaku), 2 parts by weight of Phthalocyanine Green pigment, 1 part by weight of antifoaming agent, 2 parts by weight of polysiloxane compound (trade name KS-66, manufactured by Shin'etsu Kagaku), 5 parts by weight of Bisphenol A type epoxy resin (trade name EPICLON-850, manufactured by Dainippon Ink Chemical), 15 parts by weight of talc, 40 parts by weight of barium sulfate and 2 parts by weight of finely powdered silica (trade name Aerosil #200, manufactured by Nippon Aerosil). A solder resist pattern was formed in the same manner as in Example 1. The resist pattern was further heat-cured at 150°C for 60 minutes. On the solder resist pattern thus obtained, percentage of residual film, developability, alkali resistance, solder heat resistance and solvent resistance were evaluated. Further, stability change in the lapse of time of the photosensitive resin composition was measured. The results are shown in Table 1.

Comparative Example 3

To 100 parts by weight of the solution of "Comparative Synthesis Example 3 of Photopolymerizable Resin" were added 2 parts by weight of 2-methyl-[4-(methylthio)-phenyl]-2-morpholino-1-propane (trade name Irgacure 907, manufactured by Ciba Geigy), 2 parts by weight of diethylthioxanthone (trade name Cayacure DTEX, manufactured by Nippon Kayaku), 1 part by weight of isoamyl p-methyl-aminobenzoate (trade name Cayacure DMBI, manufactured by Nippon Kayaku), 2 parts by weight of Phthalocyanine Green pigment and 1 part by weight of antifoaming agent. After kneading the composition with a triple roll, the composition was coated on a 0.03 mm polyester (PET) film with applicator so as to give a dry film thickness of 50 μm and dried at 80°C for 20 minutes to obtain a dry film resist. The dry film resist was thermally contact-bonded on a substrate with laminator, and exposed to light and developed in the same manner as in Example 1 to form a resist pattern. On the resist pattern thus obtained, percentage of residual film, developability and etching resistance were evaluated. Further, stability change with time of the dry film was measured. Further, dry film resist was thermally contact-bonded to substrate and wholly exposed to light, and its adhesive property was measured. The results are shown in Table 1.

Comparative Example 4

To 100 parts by weight of the solution of "Comparative Synthesis Example 3 of Photopolymerizable Resin" were added 2 parts by weight of 2-methyl-[4-(methylthio)-phenyl]-2-morpholino-1-propane (trade name Irgacure 907, manufactured by Ciba Geigy), 2 parts by weight of diethylthioxanthone (trade name Cayacure DTEX, manufactured by Nippon Kayaku), 1 part by weight of isoamyl p-methyl-aminobenzoate (trade name Cayacure DMBI, manufactured by Nippon Kayaku), 2 parts by weight of Phthalocyanine Green

pigment, 1 part by weight of antifoaming agent, 2 parts by weight of polysiloxane compound (trade name KS-66, manufactured by Shin'etsu Kagaku), 5 parts by weight of Bisphenol A type epoxy resin (trade name EPICLON-850, manufactured by Dainippon Ink Chemical), 15 parts by weight of talc, 40 parts by weight of barium sulfate and 2 parts by weight of finely powdered silica (trade name Aerosil #200, manufactured by Nippon Aerosil). After kneading the composition with a triple roll, the composition was coated on a 0.03 mm polyester (PET) film with applicator so as to give a dry film thickness of 50 μm and dried at 80°C for 20 minutes to obtain a dry film solder resist. Then the dry film solder resist was thermally contact-bonded to a substrate by means of a laminator and exposed to light and developed in the same manner as in Example 1 to prepare a solder resist pattern. On the resist pattern thus obtained, percentage of residual film, developability, alkali resistance, solder heat resistance and solvent resistance were evaluated. Further, stability change in the lapse of time of the dry film solder resist was measured, and adhesive property was evaluated on a film prepared by thermally contact-bonding the dry film solder resist to a substrate and wholly exposing it to light. The results are shown in Table 1.

Comparative Example 5

To 100 parts by weight of the solution of "Comparative Synthesis Example 3 of Photopolymerizable Resin" were added 2 parts by weight of 2-methyl-[4-(methylthio)-phenyl]-2-morpholino-1-propane (trade name Irgacure 907, manufactured by Ciba Geigy), 2 parts by weight of diethylthioxanthone (trade name Cayacure DTEX, manufactured by Nippon Kayaku), 1 part by weight of isoamyl p-methyl-aminobenzoate (trade name Cayacure DMBI, manufactured by Nippon Kayaku), 2 parts by weight of Phthalocyanine Green

pigment, 1 part by weight of antifoaming agent and 10 parts by weight of trimethylolpropane triacrylate. A resist pattern was formed in the same manner as in Comparative Example 1. On the resist pattern thus obtained, percentage of residual film, developability, alkali resistance and etching resistance were evaluated. Further, stability change in the lapse of time of the photosensitive resin composition was also measured. The results are shown in Table 1.

Comparative Example 6

To 100 parts by weight of the solution of "Comparative Synthesis Example 3 of Photopolymerizable Resin" were added 2 parts by weight of 2-methyl-[4-(methylthio)-phenyl]-2-morpholino-1-propane (trade name Irgacure 907, manufactured by Ciba Geigy), 2 parts by weight of diethylthioxanthone (trade name Cayacure DTEX, manufactured by Nippon Kayaku), 1 part by weight of isoamyl p-methyl-aminobenzoate (trade name Cayacure DMBI, manufactured by Nippon Kayaku), 2 parts by weight of Phthalocyanine Green pigment, 1 part by weight of antifoaming agent, 5 parts by weight of trimethylolpropane triacrylate, 2 parts by weight of polysiloxane compound (trade name KS-66, manufactured by Shin'etsu Kagaku), 5 parts by weight of Bisphenol A type epoxy resin (trade name EPICLON-850, manufactured by Dainippon Ink Chemical), 15 parts by weight of talc, 40 parts by weight of barium sulfate and 2 parts by weight of finely powdered silica (trade name Aerosil #200, manufactured by Nippon Aerosil). After kneading the composition with a triple roll, the composition was coated on a 0.03 mm polyester (PET) film with applicator so as to give a dry film thickness of 50 μm and dried at 80°C for 20 minutes to obtain a dry film solder resist. Then the dry film solder resist was thermally contact-bonded on a substrate by means of a laminator and exposed to light and developed in the same manner as in Example 1 to form a solder resist pattern. On

the resist pattern thus obtained, percentage of residual film, developability, alkali resistance, solder heat resistance and solvent resistance were evaluated. Further, stability change in the lapse of time of the dry film solder resist was measured, and adhesive property was evaluated on a film prepared by thermally contact-bonding the dry film solder resist to a substrate and wholly exposing it to light. The results are shown in Table 1.

Comparative Example 7

To 100 parts by weight of the solution of "Comparative Synthesis Example 4 of Photopolymerizable Resin" were added 2 parts by weight of 2-methyl-[4-(methylthio)-phenyl]-2-morpholino-1-propane (trade name Irgacure 907, manufactured by Ciba Geigy), 2 parts by weight of diethylthioxanthone (trade name Cayacure DTEX, manufactured by Nippon Kayaku), 1 part by weight of isoamyl p-methyl-aminobenzoate (trade name Cayacure DMBI, manufactured by Nippon Kayaku), 2 parts by weight of Phthalocyanine Green pigment and 1 part by weight of antifoaming agent. Thus, a photosensitive resin composition was obtained. A resist pattern was formed therefrom in the same manner as in Example 1. The resist pattern thus formed was further heat-cured at 150°C for 60 minutes. On the resist pattern thus obtained, percentage of residual film, developability, alkali resistance and etching resistance were evaluated. Further, stability change in the lapse of time of the photosensitive resin composition was also measured. The results are shown in Table 1.

Table 1

	Example					Comparative Example						
	1	2	3	4	5	1	2	3	4	5	6	7
Percentage of residual film	O	O	O	O	O	X	X	X	X	O	O	O
Developability	O	O	O	O	O	O	O	O	O	O	O	X
Stability with time of photo-sensitive resin composition	O	O	—	—	O	O	O	—	—	X	—	X
Stability with time of dry film	—	—	O	O	—	—	—	O	O	—	X	—
Etching resistance	O	—	O	—	O	X	—	X	—	O	—	O
Alkali resistance	—	O	—	O	—	—	X	—	X	X	O	X
Adhesiveness	—	O	O	O	—	—	—	X	X	—	O	—
Solder heat resistance	—	O	—	O	—	—	X	—	X	—	O	—
Solvent resistance	—	O	—	O	—	—	X	—	X	—	O	—

The performances shown in the tble were evaluated according to the following methods:

Percentage of residual film: Film thickness was measured before and after development; O Thickness after development was no less than 90% of the thickness before development; X Thickness after development was less than 85% of the thickness before development.

Developability: The period of time necessary for development was measured; O No more than one minute; X No less than 3 minutes.

Stability with time of photosensitive resin composition: After an accelerated stability test for 30 days in oven kept at 40°C, the state of photosensitive resin composition was

visually examined; O Composition could be developed smoothly without gelation; X Gelation of composition took place.

Stability with time of dry film: After an accelerated stability test for 30 days in oven kept at 40°C, the state of dry film was visually examined; O No cold flow was noticeable at all on dry film; X Cold flow occurred.

Etching resistance: After immersion in aqueous ferric chloride solution for 10 minutes, the shape of pattern was visually examined; O Highly reproducible copper wiring pattern was obtained without permeation of etching solution; X Thinning of copper wiring occurred due to permeation of etching solution.

Alkali resistance: After immersion in 10% aqueous solution of sodium hydroxide for 60 minutes, the state of photosensitive resin film was visually examined; O No change was noticeable; X Photosensitive film was swollen with partial peeling.

Adhesiveness: After dipping test piece in solder bath at 260°C for 10 seconds, checker-wise cuttings were given to test piece according to JISD-O-202, peeling test was carried out with cellophane adhesive tape, and occurrence of peeling was examined; O No break-off nor peeling was observed in the pattern; X Break-off or peeling was observed in a part of pattern.

Solder heat resistance: After coating a flux, test piece was dipped in a solder bath kept at 260°C for 10 seconds. After repeating the dipping five times, the state of photosensitive film was visually examined; O No change was observed even after three times repeating the dipping; X After one dipping, peeling was observed in a part of the cured photosensitive resin layer.

Solvent resistance: After immersing test piece in methylene chloride for 30 minutes, the state of cured

photosensitive resin layer was visually examined; O No change was noticeable; X Photosensitive layer was swollen.

It is apparent from Table 1 that the photosensitive resin composition of the present invention is excellent in percentage of residual film, developability, time stability of photosensitive resin composition, etching resistance, alkali resistance, adhesiveness, solder heat resistance and solvent resistance.

[Effect of the Invention]

The photosensitive resin composition of the present invention is excellent in heat resistance and chemical resistance which are both required of a photosensitive resin composition, excellent in adhesiveness to substrate, and developable with water or dilute alkaline aqueous solutions. Accordingly, the photosensitive resin composition of the present invention is usable as etching resist for copper wiring pattern, dry film resist, solder resist, etc. without exercising adverse influence on working and natural environments.